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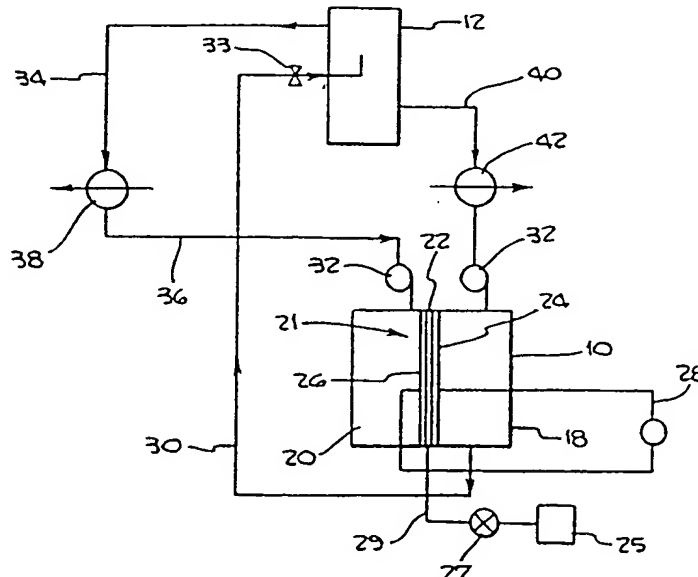
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(54) Title: GAS-PERMEABLE AND ION-PERMEABLE MEMBRANE FOR ELECTROCHEMICAL SYSTEM



(57) Abstract

An electrode apparatus adapted for use in electrochemical systems (10) having an anode compartment (20) and a cathode compartment (18) in which gas and ions are produced and consumed in the compartments during generation of electrical current. The electrode apparatus includes a membrane (22) for separating the anode compartment from the cathode compartment wherein the membrane (22) is permeable to both ions and gas. The cathode (24) and anode (26) for the assembly are provided on opposite sides of the membrane (22). During use of the membrane-electrode apparatus in electrochemical cells, the gas and ions generated at the cathode (24) or anode (26) migrate through the membrane (22) to provide efficient transfer of gas and ions between the anode compartment (20) and cathode compartment (18).

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1 Gas-permeable and ion-permeable membrane for
electrochemical system.

5 This invention was made with United States Government
support under Contract No. EG-77-C-01-4042 awarded by the
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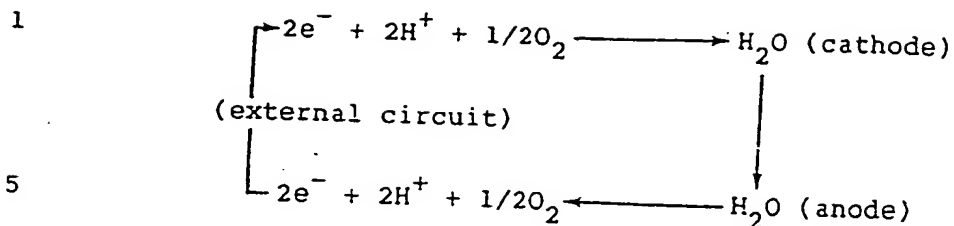
10 BACKGROUND OF THE INVENTION

1. Field of the Invention

15 The present invention relates generally to batteries
and systems which convert chemical energy into electrical
energy by use of a continuous concentration
electrochemical cell. More specifically, the present
invention relates to an improved gas-permeable electrode
for use in such systems.

20 2. Description of the Background Art

U.S. Patent No. 3,231,426, issued January 25, 1966,
discloses a continuous concentration cell in which a
voltage is obtained and an electric current is generated
25 between a cathode immersed in concentrated sulfuric acid
and an anode immersed in dilute sulfuric acid. The
reaction cycle which is set up between the electrodes is:



During operation of the cell, the concentrated sulfuric acid solution is diluted by water generated at the cathode, while the dilute sulfuric acid solution becomes more concentrated due to the generation of acid at the anode. The difference in acid concentration between the two solutions must be maintained in order to provide continuous generation of electrical energy. The system disclosed in U.S. Patent No. 3,231,426 maintains the acid concentration gradient by heating the concentrated acid solution to distill off water generated at the cathode. The water which is continuously distilled from the concentrated acid solution is cycled to the dilute acid solution to continually provide dilution of the acid which is generated at the anode. Continuous concentration cells of the type described above utilize porous electronically non-conducting beds or barriers between the electrodes which typically are made from felted asbestos fibers, glass fibers or ceramic compositions such as alumina, zirconium oxide, ion exchange membranes, or porous organics, such as polypropylene or cellulose.

Another type of thermoelectrochemical system has been developed which functions as a low-temperature power converter in which the electrochemical cell reactants are thermally regenerated at a temperature below about 250°C.

This type of thermoelectrochemical system basically includes an electrochemical cell having a cathode compartment and an anode compartment. The two compartments have a common ion permeable separation wall

1 which allows ions to pass between the two compartments but
prevents the passage of gas. A hydrogen ion reacting
cathode and a hydrogen ion reacting anode are located
within their respective compartments with the cathode and
5 anode being connectable externally from the system for
generation of an electrical voltage and current between
the electrodes.

A cathode fluid comprising a chosen Bronsted acid is
typically located in the cathode compartment and in
10 contact with the cathode. During one method of operation
of the system, hydrogen gas is generated or collected at
the cathode and the acid is consumed. The system further
includes an anode fluid comprising a chosen Bronsted base
which is located in the anode compartment and in contact
15 with the anode. During one method of operation of the
system, a cation of the base is generated and the base and
hydrogen gas are consumed at the anode. At least one of
the components, i.e., acid or base, comprises an organic
material.

20 Because of the gas-impermeability of the ion-permeable
separation wall, any hydrogen gas generated at the cathode
during operation of the system is transferred externally
to the anode compartment for consumption at the anode
during generation of the electrical current. In addition,
25 during operation of the system, the anions of the acid
and/or the cations of the base migrate through the ion
permeable separation wall into the anode or cathode
compartment, respectively, where they combine with the
cation of the base or the anion of the acid to form the
30 corresponding salt. A feature of this system is that the
salt is capable of being thermally decomposed at a
temperature below about 250°C to directly form the acid
and base as two decomposition products. These products
35 can be separated to regenerate the acid and base.

1 A thermal regenerator is provided in these systems for
thermally converting the salt directly to the acid and
base starting materials, at a temperature below about
250°C. Means for transferring the salt from the anode
5 and/or cathode compartment to the thermal regenerator are
also provided. Anode recycle means are provided for
transferring the base formed in the thermal regenerator
back to the anode compartment to replenish the base
consumed during operation of the system. Cathode recycle
10 means are also provided for transferring the acid formed
in the thermal regenerator back to the cathode compartment
to replenish the acid consumed during operation of the
system.

The above-described systems are particularly useful
15 because their relatively low operating temperatures (i.e.
below 250°C) allow them to be used in recovering waste
heat in the form of electric power from internal
combustion engines, industrial processes, and the like.
They can also be used to convert heat from other sources
20 such as solar energy, fossil or nuclear fuel, oil well
heads or other geothermal heat sources.

An important consideration in thermoelectrochemical
systems, as well as electrochemical systems, in general,
is the overall efficiency of the system and the useful
25 life. It is therefore desirable to continually search for
improvements to such systems in which the performance,
efficiency and life of the system are maximized.

SUMMARY OF THE INVENTION

30 In accordance with the present invention, a means is
provided for improving the performance, reliability, and
efficiency of electrochemical systems by reducing the
complexity and internal electrical resistance of such
35 systems.

The present invention involves the discovery that suitable separation walls between the cathode and anode compartments can be made which are permeable to both ions and gas. The provision of a gas-permeable and ion-permeable separation wall or membrane eliminates the need for externally transferring gases between the two compartments. This elimination of external gas transfer in accordance with the present invention reduces the internal resistance of the system and increases the efficiency of electrical and gas transfer between the anode and cathode compartments.

The present invention is based on an electrode apparatus which is adapted for use in electrochemical systems having anode and cathode compartments wherein the apparatus includes an anode and cathode between which is located a membrane having a cathode side and an anode side and wherein the membrane includes both ion-permeable and gas-permeable regions to provide transfer of ions and gas between the cathode and anode.

The electrode apparatus of the present invention has application to any electrochemical system in which gas must be passed between the anode and cathode and may be used in place of existing membrane barriers or other barriers designed to provide selective passage of ions between anodes and cathodes. The invention is especially well suited for use in the continuous concentration systems or acid/base systems described above.

The electrode apparatus of the present invention is based upon the use of an ion-permeable and gas-permeable membrane as the separator wall or barrier between the anode and cathode compartments of an electrochemical cell. It is preferred that the cathode and anode be placed as close to the membrane separator wall as possible in order to reduce the internal resistance of the cell due to ion migration through the electrolyte solutions and to

1 reduce the distance that gas must move from its reaction
site to or from the gas passage pores in the membrane. As
a particular feature of the present invention, the anode
and cathode are provided as porous coatings or thin layers
5 contacting opposite sides of a gas- and ion-permeable
membrane. This reduces the internal resistance of the
cell because the ions and gas generated at the electrodes
do not have to travel through any extensive distance in
the liquid phase to reach the opposite electrode.

10 These and many other features and attendant advantages
of the present invention will become apparent as the
invention becomes better understood by reference to the
following detailed description when considered in
conjunction with the accompanying drawings.

15 BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 is a schematic representation of an exemplary
thermoelectrochemical system utilizing the present
20 invention.

FIG. 2 is a cross-sectional representation of a
preferred electrode apparatus in accordance with the
present invention.

25 FIG. 3 is a cross-sectional representation of an
alternate preferred electrode apparatus in accordance with
the present invention.

DETAILED DESCRIPTION OF THE INVENTION

30 An exemplary system in which the gas-permeable and
ion-permeable membrane of the present invention can be
used is shown in FIG. 1. The system basically includes an
electrochemical cell 10 and a thermal regenerator 12.
However, it is to be understood that the present invention
35 is not limited to a thermoelectrochemical system, but may

1 be used in any electrochemical system as generally
indicated at 10 in FIG. 1.

5 The electrochemical cell 10 includes a cathode
compartment 18 and an anode compartment 20. The cathode
and anode compartments 18 and 20 are separated by a
preferred exemplary electrode apparatus as shown generally
at 21. The electrode apparatus 21 includes a central
membrane 22 which is permeable to both gas and ions. The
membrane 22 is located between and in contact with an
10 anode 26 and a cathode 24.

The requirements for membrane 22 are that it must be a
permeable membrane or barrier which allows cation and/or
anion exchange (i.e., a cation-exchange membrane, an
anion-exchange membrane or a microporous membrane for
15 cation and anion exchange), while at the same time
allowing gas transfer. The choice of the ion selectivity
of the membrane depends on the particular electrochemical
cell reaction of interest. In accordance with the present
invention, gas- and ion-permeable regions coexist in the
20 membrane. The permeability of these regions depends on
the diameter of the "pores" in these regions and the
degree of hydrophobicity of the walls of the pores. In
addition, the cell liquids in the anode and cathode
compartments must have sufficiently high surface tensions
25 so that the hydrophobic material is not wetted by the
liquids. Organic systems containing enough water or other
high surface tension solvent to give surface tensions in
excess of about 35 dynes per centimeter have been found to
be suitable. Thus, in accordance with the present
30 invention, high surface tension liquids are excluded from
the small pores of the membrane. Consequently, liquid
ionic solutions will not pass through the small pores,
whereas gas is able to pass through the small pores. As
the pore size is increased, the hydrophobicity of the
35 walls exerts less effect, and the liquid ionic solutions

1 can pass through the larger pores. While it is
advantageous to have both hydrophobic and hydrophilic
regions in close proximity in the membrane, a purely
hydrophobic material can be used if it has a sufficient
5 distribution or dispersion in the diameters of its pores.
A large hydrophobic pore will not exclude liquid, whereas
a small hydrophobic pore will exclude liquid.

Suitable membranes or barriers which provide the
desired ion- and gas-permeability can be made in a number
10 of different ways. For example, a mesh, cloth, paper,
porous film or felt of gas-permeable hydrophobic materials
having openings or pores of varying size can be used to
provide a barrier wherein gas is transported through the
smaller diameter pores or passages in the fiber mesh,
15 cloth, paper, felt or porous film and the ions are allowed
to pass through the larger openings in the mesh, cloth,
paper, felt, or porous film. Suitable materials for
forming such a mesh, cloth, paper, porous film, or felt
include non-conducting carbon fiber, expanded teflon, or
20 porous polypropylene. (Teflon is a polytetrafluoro-
ethylene manufactured by E.I. DuPont de Nemours of
Wilmington, Delaware.) The term "porous teflon" as used
herein is intended to include "expanded teflon," as is
known in the art. The selected material should have a
25 fine porosity, with sizes below 10 micrometers being
preferred. For example, when using expanded teflon, the
preferred pore size is within the range of about 1 to 3
micrometers. For Celgard 2400 and 2500, preferred pore
sizes are about 0.02 and 0.4 micrometers, respectively.
30 The actual fiber size and the size of the openings through
the mesh can be varied depending upon the particular
electrochemical cell, to provide desired rates of gas or
ion transfer.

Alternatively, suitable membranes can be formed from a
35 felt, mesh, cloth, paper or porous film of gas-permeable

1 fibers or matrices, impregnated with an ion-exchange
membrane material. Examples of the latter are specified
below. Suitable matrices or fibers include electronically
5 non-conducting carbon fiber, and expanded teflon or porous
polypropylene matrices. In such a membrane, the gas
passes through the fiber or matrix while the ions pass
through the ion-exchange regions.

Suitable membranes can also be made by treating
gas-permeable membranes so as to provide regions within
10 these otherwise ion-impermeable membranes through which
ions can be transported. For example, hydrophobic
polypropylene, such as that marketed by Celanese Corp.
(Charlotte, North Carolina) as Celgard 2500, can be
treated with drops of a solution of a cation or anion
15 exchange membrane material which, when cured, provides
ion-permeable regions at selected spaced locations in the
otherwise ion-impermeable material. Solutions of such ion
exchange membrane materials are available commercially,
for example, from Solution Technology, Inc. of Mendenhall,
20 Pennsylvania. An exemplary material is Nafion. Nafion is
a trademark of E.I. DuPont de Nemours of Wilmington,
Delaware, for a polymer of polytetrafluoroethylene with
fluorinated ether side chains terminated with sulfonic
acid groups. Another exemplary material is an
25 alkali-resistant copolymer of vinyl chloride and
acrylonitrile with quaternary nitrogen groups, available
from Ionics, Inc. of Watertown, Massachusetts. The
preferred procedures for preparing the gas- and ion-
permeable membranes are discussed in detail below. In
30 addition to polypropylene, other membrane materials can be
used such as microporous polytetrafluoroethylene (PTFE).

Other suitable membranes for practicing the present
invention can be made by treating hydrophobic membranes
with hydrophilic surfactants so as to provide ion-
35 permeable regions within these otherwise gas-permeable

1 (ion-impermeable) membranes. For example, hydrophobic
polypropylene, such as that marketed by Celanese Corp.
(Charlotte, North Carolina) as Celgard 2400, can also be
made hydrophilic by treatment with a surfactant, and this
5 product is sold as Celgard 3400. By surfactant treatment
at selected spaced locations in the otherwise ion-
impermeable material, both liquid and gas can be
transported through the modified membrane.

As yet another alternative, suitable membranes for
10 practicing the present invention may be made by providing
openings or holes in an ion exchange membrane such that
gas but not ions can pass through the holes. The size and
distribution of the holes can be determined for each
particular electrochemical system used. Optionally, the
15 membrane may be provided as a porous woven material, such
as porous woven Nafion, obtained from E.I. DuPont of
Wilmington, Delaware, and the gas passes through the
openings in the woven material.

The membrane 22 is preferably as thin as possible
20 without jeopardizing the structural integrity of the
membrane. Membrane thicknesses on the order of about 1 to
10 mils (0.025 to 0.25 mm) have been found satisfactory
and thicknesses of less than 5 mils (0.125 mm) are
desirable.

25 The relative size of the areas of gas permeability and
ion permeability in the membrane along with respective
permeabilities can be varied to suit the particular
electrochemical cell and the required ion and gas
transport. The degree of either gas or ion transport must
30 be sufficient to avoid large current-resistance (IR) drops
through the membrane or significant concentration
polarization in either the anode or cathode compartment.

Both the cathode 24 and the anode 26 are hydrogen
electrodes (i.e., electrodes which react with hydrogen gas
35 or hydrogen ions) and are porous to allow the passage of

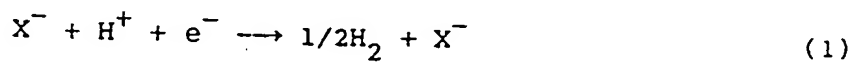
1 gas and ions through the electrode. One type of hydrogen
electrode comprises a platinized porous carbon - teflon
fuel cell electrode and is known in the art and
commercially available. Another type of hydrogen
5 electrode comprises a fine-mesh screen of tantalum,
stainless steel, or other non-corrosive metal covered with
platinum black. Still another type of hydrogen electrode
is referred to as a solid polymer electrolyte (SPE)
electrode and comprises a structure in which
10 electrocatalyst is bonded directly to both sides of a
solid polymer ionomer membrane to form the cathode and
anode. In one method of construction of an SPE electrode,
the catalyst in the form of a fine powder is mixed with
teflon emulsion solution and sintered at about 345°C.
15 The sintered teflon-bonded catalyst is then bonded to the
SPE membrane at elevated temperature and under pressure.
Another SPE electrode construction comprises the sintering
of a porous electrode using material made from carbon or
graphite powder and PTFE mixed with a platinum catalyst or
20 PTFE alone mixed with a platinum catalyst. This porous
electrode material is preferably placed in direct contact
with the membrane so that the membrane 22 is sandwiched
between the two electrodes 24 and 26. This electrode
material can also be bonded to both sides of the membrane
25 with heat and pressure and/or glued to the membrane using
ion exchange solutions, such as from Solution Technology,
Inc., or prepared by known processes, such as described by
Moore and Martin in Analytical Chemistry, Vol. 58, 1986,
pages 2569-2570. In accordance with the present
30 invention, the porosity of the electrode material must be
sufficient to allow transport of ions and gas while still
providing the desired cathode or anode functions. Since
the electrode is depolarized both from the back (solution
side) and from the front (membrane side), the electrode
35

I must be thin enough so this dual polarization can be kept to a minimum. A thickness of less than 20 mils (0.5 mm) is desirable.

5 The hydrogen gas necessary for operation of the hydrogen electrode is introduced into the electrode apparatus 21 from hydrogen reservoir 25 by way of control valve 27 and transfer line 29. Generally, once the membrane 22 is saturated with gas, no additional gas need be supplied except that which is needed to replace gas
10 which escapes from the structure. This amount is quite small and can be made up by separating escaped gas from the liquid streams. In an optimized system this amount should be zero.

15 Referring again to the overall system of FIG. 1, the cathode compartment 18 includes a cathode fluid which is in contact with cathode 24. In a preferred thermoelectrochemical system, the cathode fluid is typically a Bronsted acid, i.e., a proton donor. The acid is chosen so that the anion of the acid combines with the
20 cation of the base to form a salt which can be thermally decomposed at a temperature below about 250°C to directly form the acid and base as two decomposition products which can be separated to regenerate the acid and base starting materials for the electrochemical cell
25 reaction.

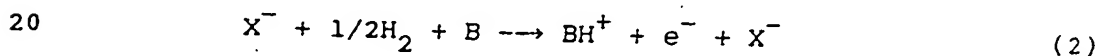
The cell reaction of the acid at the cathode 24 is shown in Equation (1) below, where hydrogen gas is generated or collected and acid is consumed at the cathode. The anion of the acid may have a valence other
30 than that indicated in Equation (1).



where X^- = anion of acid

1 Acids which are used in this particular system include
inorganic acids such as concentrated hydrochloric acid or
phosphoric acid and organic acids such as methylsulfonic
acid, trifluoromethylsulfonic acid, acetic acid, benzoic
5 acid, and the borate ester formed by condensation of boric
acid with ethylene glycol. A solvent may optionally be
used with the acid.

10 An anode fluid is located in the anode compartment 20
for contact with anode 26. The anode fluid for a
preferred thermoelectrochemical system is typically a
Bronsted base, i.e., a proton acceptor. The base is
chosen so that the cation of the base combines with the
anion of the acid to form a salt which can be thermally
decomposed at a temperature below about 250°C to form
15 two separable decomposition products and regenerate the
acid and base, as previously discussed. The cell reaction
of the base at a hydrogen anode is shown in Equation (2)
below.



where X^- = anion of acid

B = base

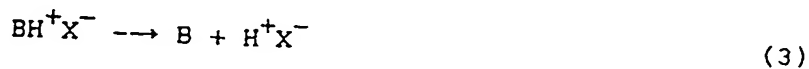
25 Thus, during the cell reaction, a cation of the base
is generated and hydrogen is consumed at the anode. Bases
which may be used in this particular system include
inorganic bases such as ammonia or phosphine, and organic
bases such as pyridine, aniline, triethanolamine,
monoethanolamine, or diethylamine. A solvent may
30 optionally be used with the base. Typically, either the
acid or the base or both comprise an organic material.

35 As shown in FIG. 1, the electrodes 24 and 26 are
connected to an external circuit schematically shown as 28
for generating an electrical current and voltage. The
external circuit 28 can include electric motors or other

1 systems for utilizing the electric energy generated by
cell 10, or batteries or other suitable systems for
storing the electric energy generated by cell 10.

5 In order to continually regenerate the acid and base
consumed during operation of cell 10, the salt formed by
the combination of the cation of the base and the anion of
the acid is thermally decomposed. To accomplish this
decomposition and regeneration, the electrolyte containing
10 the salt is removed from the cell 10 and transferred to
the thermal regenerator 12. If the salt is formed in the
anode compartment 20, the anode solution is transferred to
the thermal regenerator 12. If the salt is formed in the
cathode compartment 18, the cathode solution is
15 transferred to the thermal regenerator 12. If the salt is
formed in both the anode and cathode compartments (20,
18), both the cathode and anode solutions are transferred
to the thermal regenerator 12. For the sake of
simplicity, FIG. 1 shows only one alternative, that in
20 which the salt is formed in the cathode compartment 18,
but the apparatus may be readily modified to accommodate
the other alternatives mentioned.

In FIG. 1, the cathode solution is continually removed
from the cell via line 30 and transferred to the thermal
regenerator 12 utilizing pump 32 or other liquid transfer
25 device. The cathode solution transferred in line 30
contains the salt in a solvent in the same concentration
as present in the cathode compartment 20. In the thermal
regenerator 12, the transferred cathode solution is heated
to a temperature below about 250°C to thermally
30 decompose the salt BH^+X^- to form the acid and base, as
shown in Equation (3) below.



where B = base

35 X^- = anion of acid

1 The acid and base must be capable of being separated.
2 If either the acid or base is volatile and the other is
3 not, then the volatile component may be condensed and
4 returned to the cathode compartment 18 if it is the acid
5 or the anode compartment 20 if it is the base.

6 As shown in FIG. 1, the volatile base flows out of
7 thermal regenerator 12 into line 34 where it is cooled and
8 condensed in a condenser 38 to a temperature of about 0 to
9 80°C. The condenser 38 typically uses water or air as a
10 heat transfer means. The cooled base is then conducted
11 through line 36 into the anode compartment 20 to replenish
12 the base therein. The liquid acid component remaining in
13 the thermal regenerator 12 after heating is conducted out
14 through line 40, and optionally through cooler 42, and is
15 returned to the cathode compartment to replenish the acid
16 therein. Solvent which was not volatilized by heating in
17 the thermal regenerator 12 is carried along with the acid
18 component.

19 The thermoelectrochemical system shown in FIG. 1 may
20 be operated using a variety of acid-base systems.
21 Examples of such systems include, but are not limited to,
22 those listed below.

- 23 a. Pyridine - methanesulfonic acid
- 24 b. Pyridine - hydrochloric acid
- 25 c. Pyridine - phosphoric acid
- 26 d. Pyridine - trifluoromethanesulfonic acid
- 27 e. Acetic acid - triethanolamine
- 28 f. Acetic acid - monoethanolamine
- 29 g. Acetic acid - diethylamine
- 30 h. Acetic acid - pyridine
- 31 i. Benzoic acid - ammonia
- 32 j. Aniline - hydrochloric acid
- 33 k. Ammonia - borate ester [condensation product of
34 boric acid and ethylene glycol]
- 35 l. Lactic acid - diethylamine

1 An exemplary electrode apparatus in accordance with
the present invention is shown generally at 50 in FIG. 2.
The apparatus 50 includes a central membrane 52 which can
5 be made from electronically non-conductive carbon felt
which is available from Fiber Materials, Inc. (Biddeford,
Maine). The carbon felt which functions as membrane 52 is
a very fine mesh felt material. It is believed that gas
passes through or along the carbon fibers, to provide gas
permeable regions in membrane 52. The openings between
10 the fibers of the carbon felt are filled with a cation
exchange material such as Nafion, for example, by adding
the felt to a 5% solution of Nafion and boiling the
solution to dryness. The Nafion regions in the felt
function as the ion permeable regions when the membrane is
15 saturated with solution during use as electrode apparatus
21 in an electrochemical cell such as 10 shown in FIG. 1.
The composite carbon felt-Nafion membrane may be
visualized as a Nafion membrane having carbon fibers
extending from one edge of the membrane to the other.

20 Anode means are provided on a first side of
membrane 52. The anode means includes a layer of porous
electrode material 54 comprising a carbon-teflon mixture
impregnated with approximately 0.25 mg/cm^2 of platinum.
Other porous hydrogen electrode materials can be utilized
25 provided they have sufficient porosity to allow migration
of gas and ions through the anode while providing desired
hydrogen electrode characteristics. The porous layer 54
can be prepared, for example, by separating the catalyst
layer from the hydrophobic backing of a fuel cell
30 electrode manufactured by Energy Research Company
(Danbury, Connecticut). This separated catalyst layer is
then pressed against the first side of membrane 52.
Optionally, a porous electrode may be formed by depositing
platinum black on a fine metal screen.

35

1 Current collector means for collecting current from
the anode porous layer 54 are provided by, for example, a
layer of electronically conductive graphite felt 56 and/or
5 gold plated fifty mesh screen 58 formed of tantalum,
stainless steel, or other non-corrosive metal. The
graphite felt layer 56 may be type VDG which is available
from Union Carbide Company, New York, New York. Cathode
means are provided on the second side of membrane 52. The
cathode means includes the same layers as the anode
10 means. These layers include porous electrode material
layer 60, conductive carbon felt layer 62 and current
collector screen 64. The electrode apparatus shown in
FIG. 2 was tested as described in Example 1 herein.

15 A second exemplary electrode apparatus in accordance
with the present invention is shown generally at 70 in
FIG. 3. The apparatus 70 is the same as apparatus 50 in
FIG. 2 in that it includes a central gas- and ion-
permeable membrane 72, porous anode layer 74, porous
cathode layer 76 and current collectors 78 and 80. In
20 this embodiment, the membrane 72 is constructed by placing
small (1 mm) drops of five percent Nafion solution
(obtained from Solution Technology Inc., Mendenhall,
Pennsylvania) onto selected regions of a piece of
hydrophobic microporous polypropylene (Celgard 2500, from
25 Celanese Corp., Charlotte, North Carolina). The membrane
is air dried and then cured at 120°C for ten minutes.
The Nafion solution produces regions permeable to cations
as represented schematically at 82, with the remaining
gas-permeable, ion-impermeable regions of the hydrophobic
30 microporous polypropylene being represented at 84. The
porous electrode layers 74 and 76 can be made from the
same material as in apparatus 50 of FIG. 2 and the current
collectors 78 and 80 can be provided by graphite felt, for
example. The electrode apparatus 70 was tested as
35 described in Example 2 herein.

I A third exemplary electrode apparatus in accordance
with the present invention may be prepared by taking two
pieces of porous (expanded) PTFE backed fuel cell
5 electrodes from Energy Research Company and modifying
these electrodes by coating the PTFE backing with five
percent Nafion solution. The Nafion solution partially
soaks into the PTFE to provide areas of ion permeability
in the otherwise ion-impermeable PTFE layer. The two
10 electrodes are pressed together with the two PTFE surfaces
in contact. The assembly is cured at 120°C for one-half
hour to bond the two pieces together. The resulting
structure comprises a sandwich structure including, from
the outside in: (a) the two electrodes; (b) adjacent
15 regions of porous teflon containing islands of Nafion; and
(c) a central region containing islands of Nafion.
Alternatively, a Nafion-impregnated teflon composite may
be simply pressed against fuel cell electrodes. The
teflon is vacuum impregnated at 180°C with the Nafion by
20 dissolving Nafion in dimethyl sulfoxide (DMSO) and drawing
this solution into the teflon. The vacuum treatment is
continued until all of the DMSO evaporates. After the
composite has cooled, hot DMSO (110°C) is used to wipe
excess Nafion from both surfaces of the membrane
25 composite. Optionally, electrode means may be provided by
vacuum impregnating a slurry of platinized activated
carbon into the external pores (i.e. pores at or near the
surface) of both sides of the membrane composite and
bonding the electrodes to the membrane pores using Nafion
solutions.

3.0 Collector means for each electrode are provided, for
example, by tantalum screens which are embedded in the
catalyst layers. A hydrogen manifold for introducing
hydrogen gas into the membrane assembly is prepared by
bonding a non-conductive tube to one edge of the
35 assembly. RTV 3145 Sealant (from Dow Corning, Midland,

1 Michigan) can be used to seal the remaining three edges of
the assembly. This assembly and an alternative thereof
were tested as described in Examples 3 and 4 herein.

5 A fourth exemplary electrode apparatus in accordance
with the present invention may be prepared using a
commercially available porous ion-permeable membrane, such
as porous Nafion, as the separation membrane and pressing
commercially available fuel cell electrodes against the
10 membrane. The gas passes through the pores in the
membrane, while the ions pass through the membrane
itself. This type of electrode apparatus was tested as
described in Example 5.

EXAMPLE 1

15 This example illustrates the testing of the electrode
apparatus shown in FIG. 2, using a composite carbon
felt-Nafion membrane. The electrode apparatus was
constructed as previously described herein. In the first
20 test described below, methylsulfonic acid was used as the
cell fluid on both sides of the membrane. The purpose of
this initial test was to prove that both gas and ions can
be efficiently transported across the membrane. In the
second test described below, other system fluids were used
25 to provide improved efficiency in the passage of ions (or
current) and gas.

The electrode apparatus shown in FIG. 2 was tested by
immersion in a mixture of three moles water to one mole
methyl sulfonic acid ($\text{CH}_3\text{SO}_3\text{H}$). A hypodermic needle
30 was inserted into the membrane 52 to supply hydrogen
thereto from a hydrogen gas cylinder. When current was
applied to the assembly 50, hydrogen was produced at the
cathode layer 60. This hydrogen is expected to diffuse
through the membrane 52 and be consumed at the anode
35 layer 54. Simultaneously, protons diffuse through

1 membrane 52 from the anode 54 to the cathode 60.
Polarization measurements were taken with a Model 363
potentiostat/ galvanostat (obtained from Princeton Applied
Research Company, Princeton, New Jersey). Polarization
5 tests are considered to be a good indication of the
ability of an electrode apparatus to generate current when
utilized in electrochemical cells of the type shown in
FIG. 1. Since polarization represents the resistance or
inefficiency of the system, a low polarization voltage is
10 desirable. The results of the polarization tests
conducted at room temperature were as follows:

	<u>Current Density (ma/cm²)</u>	<u>Polarization (mV)</u>
15	0.2	7
	2.0	74
	20.0	580

20 The results described above are interesting, but they
do not prove that hydrogen from the cathode was passing to
the anode, since hydrogen was fed to the electrode from an
external source.

In a second test of the composite membrane electrode
apparatus of FIG. 2, lactic acid (LA) and diethylamine
25 (DEA) were used as the cell fluids. The test was
conducted as described above except that the introduction
of hydrogen through a hypodermic needle was omitted. The
cathode compartment contained an acidic mixture consisting
of 2.0:1.0:2.0 mole parts LA:DEA:H₂O, and the anode
30 compartment contained a basic mixture consisting of
1.8:1.0:5.0 mole parts DEA:LA:H₂O. The electrode
apparatus was bathed in pure H₂ at 4.2 psig prior to
filling the anode and cathode compartments with the above
liquid mixtures. It is this initially placed hydrogen
35 which is counted upon to be trapped along the carbon fiber

1 passages when the cell is filled with liquid acid and
base. Tests were started at 74°C. The open circuit
voltage was 0.29 volts. The short-circuited current
decreased from 1.5 ma/cm² to 0.2 ma/cm² after
5 60 minutes. At room temperature, currents of 0.2 ma/cm²
could also be sustained.

It appears that these results were due to hydrogen
dissolved in the cell fluids acting as a hydrogen source
to the anode rather than due to the diffusion of hydrogen
10 through the membrane from the cathode to the anode. In
addition, the lack of temperature dependence in the
experiments on the composite carbon-Nafion membrane
suggests that gas solubility and diffusion are
rate-controlling. From these results, it appears that the
15 composite carbon-Nafion membrane was not capable of
passing hydrogen gas at the fluxes required to provide an
operable system.

For purposes of comparison, the carbon felt described
above was tested without the addition of Nafion. It was
20 found that in a cell using this structure as the
separation membrane, currents could be maintained only so
long as external hydrogen was pumped in. Thus, this
structure did not allow hydrogen gas to pass through the
membrane.

25

EXAMPLE 2

This example illustrates the testing of the electrode
apparatus shown in FIG. 3. The electrode apparatus was
30 constructed as previously described herein.

The electrode apparatus shown in FIG. 3 was tested for
polarization in the same manner as described in Example 1.
The results were as follows:

35

1	<u>Current Density (ma/cm²)</u>	<u>Polarization (mV)</u>
	0.2	32
	2.0	350
5	4.0	670

The apparatus 70 operated stably at 2.0 ma/cm² with the hydrogen supply shut off. By contrast, the electrode assembly 50 shown in FIG. 2 could maintain currents only briefly once the hydrogen supply was stopped, as previously discussed.

EXAMPLE 3

15 This example illustrates the testing of the third exemplary electrode apparatus of the present invention, comprising Nafion-soaked PTFE layers bonded together. The electrode apparatus was constructed as generally described herein to provide the sandwich structure previously noted.

20 This electrode apparatus was tested for polarization in the same manner as described in Example 1. The results were as follows:

25	<u>Current Density (ma/cm²)</u>	<u>Polarization (mV)</u>
	0.2	5
	5.0	47
	50.0	377

30 This assembly operated stably for 20 minutes with the hydrogen supply shut off.

EXAMPLE 4

35 This example illustrates testing of an alternative to the third exemplary electrode apparatus of the present invention comprising a Nafion-impregnated teflon composite.

1 This electrode was constructed as follows. Expanded
teflon of 1.0 micrometer (0.0001 cm) nominal pore size was
treated with Nafion to make a Nafion-teflon composite
which contained about 35% Nafion and 65% teflon.
5 Permeability measurements showed that this composite
passed H_2 gas at a rate of $0.1 \text{ cm}^3/\text{sec. cm}^2 \text{ psi}$
where psi refers to a differential pressure of one pound
per square inch.

Electrodes were attached to the membrane composite as
10 follows. Activated carbon, sold as Black Pearls 2000 by
Cabot Company of Boston, Massachusetts, was platinized and
a slurry of the carbon was drawn into the external pores
of the membrane composite by vacuum impregnation. This
membrane composite had a thickness of approximately 15
15 mils (0.375 mm).

A 2 cm^2 electrode membrane composite combination was
mounted in a glass cell and exposed to 1 atmosphere of
hydrogen at room temperature. The anode compartment was
then filled with a 15 weight percent ammonia, 85 weight
20 percent water solution. The cathode compartment was
filled with a solution made up from 0.80 mole fraction
boric acid and 0.20 mole fraction ethylene glycol. This
mixture forms an acid containing a borate-glycol ester
anion by a condensation process involving elimination of
25 water. The open circuit voltage of this cell was
0.225 volts. The short circuit current at room
temperature was 2.0 ma/cm^2 . The current-voltage plot
was linear over the entire range.

In a separate test, electrodes were attached to the
30 membrane composite by pressing against the membrane, fuel
cell electrodes obtained from Prototech Company of Newton
Highlands, Massachusetts, and having 0.5 mg/cm^2 platinum
loading. Using the same cell fluids as noted above, this
system provided about 10 percent lower current at short
35 circuit than the previous system using activated carbon.

- 1 However, when a lactic acid-diethylamine fluid system was substituted for the borate-ammonia system, the short circuit current dropped to 0.55 ma/cm^2 .

5

EXAMPLE 5

This example illustrates the testing of the fourth exemplary electrode apparatus of the present invention comprising a porous Nafion separation membrane.

- 10 A 21-mil (0.525 mm) thick porous Nafion membrane was obtained from Solution Technology Inc. of Mendenhall, Pennsylvania. Fuel cell electrodes obtained from Prototech Company of Newton Highlands, Massachusetts and identical with those used in Example 4, were pressed
15 against the membrane. The assembly was mounted in test equipment that circulated temperature-controlled acid and base fluids past the cathode and anode respectively. The equipment also fed hydrogen or nitrogen gas to the edge of the anode. The working fluids comprised acidic and basic
20 mixtures of lactic acid and diethylamine. The acidic mixture was made up by adding 103 ml of diethylamine and 36 ml of water to 204 ml of 75% by weight aqueous solution of lactic acid. The basic mixture was made up by adding 189 ml of diethylamine and 90 ml of water to 103 ml of 75%
25 lactic acid.

- At 60°C , the initial resistance of the 2.0 cm^2 cell was 20 to 30 ohms, which was 3 to 5 times the value measured under comparable conditions with the thin Nafion-Teflon composite membrane used in Example 4. Early
30 in the experiment, the short-circuit current was 9 mA. Over a period of 18 hours, the short-circuit current gradually decayed to 0.4 mA. At this stage, the current was the same whether nitrogen or hydrogen gas was fed to the edge of the anode. Coulombic data recorded during a
35 3-hour run with the anode and cathode compartments and the

1 gas edge feed under a blanket of nitrogen showed
unequivocally that hydrogen consumed by the anode must
have travelled through the pores in the Nafion membrane.

5 This test demonstrates the viability of a cell based
on porous Nafion as the separator material. The thickness
of the available membrane, and the physical characteristics
of the electrodes prevented achievement of optimum cell
performance. Approaches for reaching optimum performance
include fabrication of thinner porous Nafion membranes and
10 the use of thinner electrodes, and better contact between
the electrodes and the membranes. For example, an
electrode apparatus could be formed as described in
Example 4 by depositing catalyst particles within the
surfaces of the membrane or as described earlier by
15 thermal compression bonding and/or curing with Nafion
solution used as a glue. By such bonding, thin catalyzed
sheet electrodes can be bonded to the membrane or
catalyzed particles within the external pore structure of
the membrane can be bonded to the membrane structure. It
20 is anticipated that with such optimization, cell
performance comparable to those discussed in Examples 2-4
can be obtained.

These results presented in Examples 2-5 indicate the
effectiveness of the electrode apparatus of the present
25 invention for providing for the transfer of both gas and
ions in an operating electrochemical cell. It is
recognized that the current obtained was lower than is
desired for an operating system. However, significant
improvements in current may readily be obtained by: (a)
30 increasing the temperature in the electrochemical cell;
(b) optimizing the contact and/or bonding between the
membrane composite and the electrodes; (c) making the
electrodes thinner, for example, within the range of 1 to
4 mils (0.0025 to 0.01 cm); (d) making the separation
35 membrane thinner; and/or (e) optimizing the electrode

1 composition and structure to accommodate liquid flow.
Thus, when used in such an optimized system it is
anticipated that the electrode apparatus of the present
invention can provide current at the levels required for
5 practical application.

Although the present invention has been described in
detail with regard to exemplary embodiments involving
acid-base type thermoelectrochemical cells, it should be
understood that the invention is not limited to use only
10 in these types of cells. Rather the present invention has
wide application to any type of electrochemical cells
where it is necessary to have combined transport of both
gas and ions between the electrodes for proper cell
operation. Those skilled in the art will recognize that
15 the within disclosures are exemplary only and that various
other alternatives, adaptations and modifications may be
made within the scope of the present invention.
Accordingly, the present invention is not limited to the
specific embodiments as illustrated herein, but is only
20 limited by the following claims.

CLAIMSWhat is Claimed is:

1. An electrode apparatus adapted for use in an electrochemical system having an anode compartment and a cathode compartment in which gas and ions are produced and consumed in said compartments during electrical current generation by said system, wherein said electrode apparatus comprises:
- a membrane for separating said anode compartment from said cathode compartment, said membrane having a cathode side and an anode side and comprising ion-permeable regions to provide transfer of ions between the cathode and anode sides of the membrane and gas-permeable regions to provide transfer of gases between the cathode and anode sides of the membrane;
- cathode means located in the cathode compartment on said cathode side of the membrane and in contact with said membrane for generating electric current; and
- anode means located in the anode compartment on said anode side of the membrane and in contact with said membrane for generating electric current wherein gas and ions generated at said cathode means and anode means migrate through said membrane to provide transfer of said gas and ions between said anode and cathode compartments.
2. An electrode apparatus according to claim 1 wherein said anode means and said cathode means comprise hydrogen electrodes and said gas comprises hydrogen.
3. An electrode apparatus according to claim 1 wherein said ion-permeable regions are provided by ion-permeable materials selected from the group consisting

5 of cation exchange materials or membranes, anion exchange materials or membranes and microporous hydrophilic membranes.

1 4. An electrode apparatus according to claim 1 wherein said gas-permeable regions are provided by a hydrophobic microporous membrane material.

1 5. An electrode apparatus according to claim 4 wherein said gas permeable material comprises hydrophobic microporous polypropylene or microporous polytetrafluoroethylene.

1 6. An electrode apparatus according to claim 1 wherein said membrane comprises an ion-permeable membrane having formed therein at selected locations gas-permeable regions.

1 7. An electrode apparatus according to claim 6 wherein said gas-permeable regions comprise openings in said ion-permeable membrane.

1 8. An electrode apparatus according to claim 1 wherein said membrane comprises a gas-permeable membrane having formed therein at selected locations ion-permeable regions.

1 9. An electrode apparatus according to claim 1 wherein said membrane comprises gas-conducting fibers in the form of a felt, said felt having ion-conducting material in the spaces between said fibers to allow passage of ions therethrough.

1 10. An electrode apparatus according to claim 9 wherein said gas-conducting fibers are selected from the

group consisting of electronically non-conducting carbon, porous polytetrafluoroethylene, and porous polypropylene.

1 11. An electrode apparatus according to claim 1
 5 wherein said membrane comprises a hydrophobic material in the form of a felt, mesh, paper, cloth or porous film having openings of relatively small and relatively large sizes to allow passage of gas through said openings of small size and passage of ions through said openings of large size.

1 12. An electrode apparatus according to claim 1
 1 wherein said cathode means comprises a layer of porous electrode material on the cathode side of said membrane.

1 13. An electrode apparatus according to claim 1
 1 wherein said anode means comprises a layer of porous electrode material on the anode side of said membrane.

1 14. An electrode apparatus according to claim 12
 1 wherein said anode means comprises a layer of porous electrode material on the anode side of said membrane.

1 15. An electrode apparatus according to claim 12
 1 wherein said cathode means includes current collector means in contact with said porous electrode material for collecting electrical current generated thereby.

1 16. An electrode apparatus according to claim 13
 1 wherein said anode means includes current collector means in contact with said porous electrode material for collecting electrical current generated thereby.

1 17. An electrode apparatus according to claim 14
 1 wherein said porous electrode material comprises a carbon-polytetrafluoroethylene mixture impregnated with platinum.

1 18. An electrode apparatus according to claim 14
wherein said porous electrode material comprises
polytetrafluoroethylene impregnated with platinum.

1 19. An electrode apparatus according to claim 15
wherein said current collector means comprises:
an electrically conductive screen; and
5 a layer of electronically conductive felt located
between and in contact with said conductive screen and
said porous electrode material.

1 20. An electrode apparatus according to claim 16
wherein said current collector means comprises:
an electrically conductive screen; and
5 a layer of electronically conductive graphite felt
located between and in contact with said conductive screen
and said porous electrode material.

1 21. An electrode apparatus according to claim 1
wherein:
a) said membrane comprises electronically
non-conductive carbon felt impregnated with a polymer of
5 polytetrafluoroethylene with fluorinated ether side chains
terminated with sulfonic acid groups; and
b) said anode means and said cathode means each
comprise:

10 1) an electrode comprising a carbon-polytetra-
fluoroethylene mixture impregnated with platinum;
2) a layer of electronically conductive graphite
felt contacting said electrode; and
3) a layer of gold plated mesh screen contacting
said electronically conductive graphite felt.

1 22. An electrode apparatus according to claim 1
wherein:

5 a) said membrane comprises hydrophobic microporous polypropylene including at selected locations regions of a polymer of polytetrafluoroethylene with fluorinated ether side chains terminated with sulfonic acid groups; and

b) said anode means and said cathode means each comprise:

- 10 1) an electrode comprising a carbon-polytetrafluoroethylene mixture impregnated with platinum; and
2) a layer of electronically conductive graphite felt contacting said electrode.

1 23. An electrode apparatus according to claim 1 wherein:

5 a) said membrane is formed from two layers of porous polytetrafluoroethylene each coated on a first side with a polymer of polytetrafluoroethylene with fluorinated ether side chains terminated with sulfonic acid groups, and bonded together on a second side opposite said first side;

b. said anode means and said cathode means each comprise:

- 10 1) an electrode comprising a carbon-polytetrafluoroethylene mixture impregnated with platinum; and
2) a layer of electronically conductive graphite felt contacting said electrode.

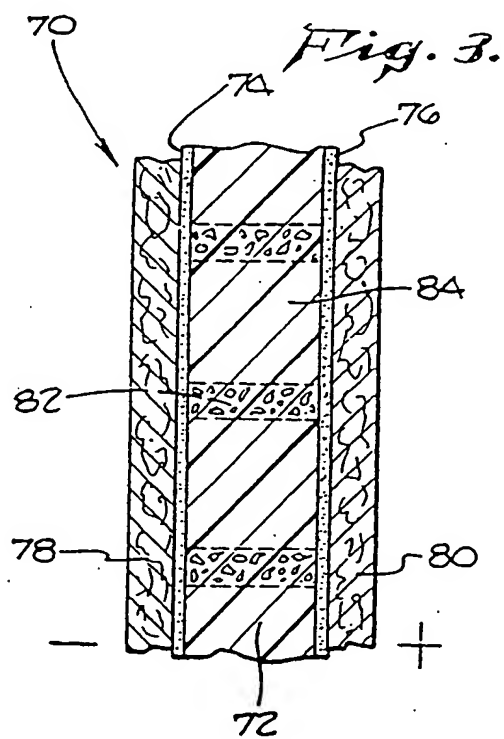
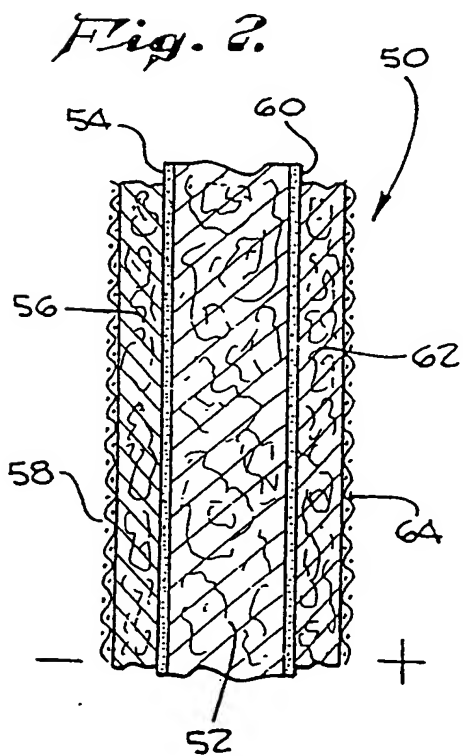
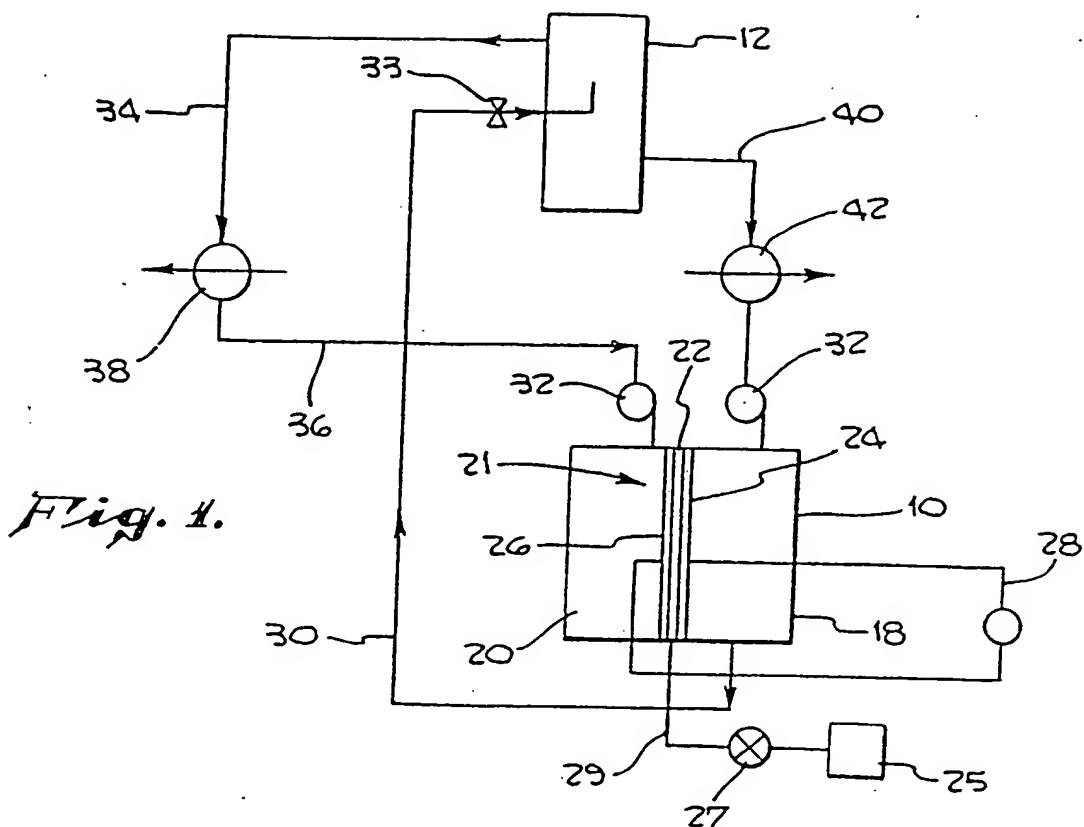
1 24. An electrode apparatus according to claim 1 wherein said membrane is bonded to said anode means and said cathode means.

1 25. An electrode apparatus according to claim 1 wherein said membrane comprises porous polytetrafluoroethylene impregnated with a polymer of polytetrafluoroethylene with fluorinated ether side chains terminated
5 with sulfonic acid groups.

1 26. An electrode apparatus according to claim 25
 wherein said anode means and said cathode means comprise a
 material selected from the group consisting of platinized
5 activated carbon particles, platinum-impregnated teflon,
 and platinum particles, located within and bonded to the
 external pores of said membrane.

1 27. An electrode apparatus according to claim 1
 wherein said electrochemical system comprises lactic acid
 and diethylamine.

1 28. An electrode apparatus according to claim 1
 wherein said electrochemical system comprises ammonia and
 borate ester.



INTERNATIONAL SEARCH REPORT

International Application No PCT/US 88/02062

I. CLASSIFICATION OF SUBJECT MATTER (If several classification symbols apply, indicate all) *		
According to International Patent Classification (IPC) or to both National Classification and IPC		
IPC ⁴ : H 01 M 8/18; //H 01 M 2/14		
II. FIELDS SEARCHED		
Minimum Documentation Searched *		
Classification System	Classification Symbols	
IPC ⁴	H 01 M	
Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched *		
III. DOCUMENTS CONSIDERED TO BE RELEVANT *		
Category *	Citation of Document, ¹¹ with indication, where appropriate, of the relevant passages ¹²	Relevant to Claim No. ¹³
A	US, A, 3231426 (F.A. LUDWIG) 25 January 1966 see figure 1; column 2, line 53-60; column 3, line 3-47; column 5, line 20-37, 49-55; claim 1	1,6,7
A	DE, A, 3302635 (BECKER FRIEDRICH) 2 August 1984 see figure 1; claim 1, page 3 last paragraph; page 4, lines 17-22	1,2,8
A	DE, A, 3239992 (BECKER FRIEDRICH) 3 May 1984 see claims 1,8,12; page 3 last paragraph; page 4, paragraph 3; page 6, lines 4-11	1,8,9,10
A	US, A, 3764387 (R.E. STACK) 9 October 1973 see figure 3, column 3, lines 44-58, column 4, lines 17-33	
A	GB, A, 1020171 (UNION CARBIDE) 16 February 1966 see claims 1,8,9	
<p>* Special categories of cited documents: ¹⁰</p> <p>"A" document defining the general state of the art which is not considered to be of particular relevance</p> <p>"E" earlier document but published on or after the international filing date</p> <p>"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)</p> <p>"O" document referring to an oral disclosure, use, exhibition or other means</p> <p>"P" document published prior to the international filing date but later than the priority date claimed</p> <p>"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention</p> <p>"X" document of particular relevance: the claimed invention cannot be considered novel or cannot be considered to involve an inventive step</p> <p>"Y" document of particular relevance: the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.</p> <p>"&" document member of the same patent family</p>		
IV. CERTIFICATION		
Date of the Actual Completion of the International Search	Date of Mailing of this International Search Report	
10th October 1988	2 NOV 1988	
International Searching Authority	Signature of Authorized Officer	
EUROPEAN PATENT OFFICE	P.C.G. VAN DER PUTTEN	

III. DOCUMENTS CONSIDERED TO BE RELEVANT (CONTINUED FROM THE SECOND SHEET)

Category *	Citation of Document, with indication, where appropriate, of the relevant passages	Relevant to Claim No
A	GB, A, 791075 (H. VOGT) 26 February 1958 see pages 2, lines 26-27, lines 84-131 ---	
A	US, A, 3438812 (S. CHERNEY et al.) 15 April 1969 see column 5, lines 13-20; column 5, line 75 - column 6, line 4 ---	
A	GB, A, 2039133 (GENERAL ELECTRIC COMP.) 30 July 1980 ---	
P,A	US, A, 4738904 (F.A. LUDWIG et al.) 19 April 1988 -----	